Studies of the Processes operative in Solutions. Part I.—*The Sucroclastic Action of Acids as influenced by Salts and Non-Electrolytes.*

By Robert John Caldwell, B.Sc. (Lond.), A.C.G.I., Leathersellers' Company's Research Fellow, Chemical Department, City and Guilds of London Institute, Central Technical College.

(Communicated by Professor H. E. Armstrong, F.R.S. Received and read June 14, 1906.)

[*International Catalogue of Scientific Literature.*

Author's title slip :—C. D.

Subject slips :—

C 0310	Hydrolysis of Sugar in relation to.
C 6240	of Acids in presence of Glucose, etc.
D 1820	Cane Sugar, hydrolysis of.
D 7090	Hydrolysis by Acids as affected by Salts.
D 7155	Hydrolysis of Sugar in relation to.
D 7275	Conductivity of Acids in presence of Glucose, etc.
Q 1424	Hydrolysis of Cane Sugar by Acids.]

The investigation of which the results are now recorded is an extension of that undertaken in conjunction with E. Frankland Armstrong in which the sucroclastic action of acids was contrasted with that of enzymes; it forms a necessary part of a larger inquiry which is being carried out at the Central Technical College in the hope of determining the precise nature of enzyme action and of hydrolytic change generally. Evidence was advanced* that the processes must be regarded as similar, notwithstanding the extraordinary difference in activity manifest on comparing the two classes of hydrolytic agents, except that and in so far as third substances produce somewhat different effects, the rate of change being modified in the case of enzymes only by substances which act selectively,† whilst in the case of acids the added substance appeared to exercise an influence which might be regarded as a concentration effect.

It is now obvious, however, that a fallacy underlay our conclusion in so far as the action of acids is concerned and that a like fallacy more or less affects, if it do not invalidate, the conclusions of previous workers in similar fields. It will be clear that to determine the influence of any added substance, this should be made the only variable at first: in point of fact, a second variable—the amount of water present—has also been introduced.

---

* 'Roy. Soc. Proc.,' 1904, vol. 73, p. 526; vol. 74, p. 195.

† *Ibid.*, vol. 73, p. 516.

Solutions have been prepared, as a rule, by dissolving the various substances to produce a given volume of solution: the result being that water has been displaced in introducing the third substance. Morse and Frazer appear to have been the first to call attention to the consequences of this practice, in the comprehensive account of their observations on "The Osmotic Pressure and Freezing Points of Solutions of Cane Sugar," published in the July number, 1905, of the 'American Chemical Journal.'* They have shown, at least in the case of cane sugar, that the normal standard volume for osmotic pressure is not that of a gramme-molecular proportion of substance dissolved in water to a volume of 1 litre; the true standard, instead of being such a volume-normal solution, is the weight-normal solution (as they term it) obtained by dissolving a gramme-molecular proportion of the substance in 1 litre of water; such a solution exercises an osmotic pressure approximately equal to the pressure exerted by a gramme-molecular proportion of hydrogen reduced to 1 litre.

The need of maintaining the proportions of water and acid as well as that of the hydrolyte constant throughout the experiments, *so that the amount of the added substance should be the only variable*, was contemplated at the outset of this inquiry; indeed it was undertaken from this point of view at Professor Armstrong's request, before my attention had been directed to Morse and Frazer's communication.†

The experiments now described have shown that cane sugar itself and several other carbohydrates have a relatively small although very distinct concentrating effect; alcohol, however, has a marked inhibiting effect—probably because it enters into competition with the water and withdraws hydrogen chloride from it; glycerol occupies an intermediate position between alcohol and the carbohydrates: in other words, non-electrolytes

---

* Vol. 34, pp. 28—91.

† In discussing the influence of concentration of the hydrolyte on the rate at which milk sugar is hydrolysed (Armstrong and Caldwell, *op. cit.*, p. 531), results were quoted referring to volume-normal solutions containing 9, 18 and 27 grammes of lactose in 100 c.c. Such solutions contain very different amounts of water, viz. :—

9 grammes lactose.	91·44 grammes water.
18 " "	85·82 " "
27 " "	79·96 " "

The great increase observed in the rate of change is to be attributed mainly to the displacement of water; on reference to Table I it will be seen that the corresponding volume-normal solutions of cane sugar contain a larger proportion of water; the greater influence of changes in concentration on the rate at which milk sugar undergoes hydrolysis in comparison with cane sugar, referred to in the paper under consideration (p. 531), is probably more apparent than real, but the subject is one which needs further experimental investigation.

have comparatively little influence in promoting hydrolysis. The weak electrolyte acetic acid also has but little influence. Metallic salts accelerate the rate of change, the influence of those derived from monad metals being already considerable and that of salts derived from dyads at least twice as great; it will be contended that their activity is due to their dehydrating influence.

The literature relating to the action of acids on cane sugar is extraordinarily voluminous, at least 140 papers having been published which bear on the subject. As the writer is engaged in preparing for the British Association a report summarising the work which has been done, it will be unnecessary to consider at length the arguments which have been advanced. Ostwald, besides carrying out a series of observations on the action of a variety of acids on cane sugar, which led him to conclude that the activity of the several acids was of the same order as that established by other methods, especially by the determination of their electrical conductivity, also made a few experiments on the influence of the concentration of the sugar on the rate of hydrolysis. The results he obtained led him to infer, in the case of chlorhydric acid, that the amount of sugar hydrolysed in unit time increased rapidly, out of all proportion to the increase in the concentration of the sugar. On altering the concentration of the acid, maintaining that of the sugar constant, he noticed a similar lack of proportionality between the rate of inversion and the amount of acid present, the acid being less active in dilute than in strong solution: according to his method of stating the case, whereas the molecular conductivity of the acid diminishes as its concentration is increased, its molecular sucroclastic activity increases as it is increased in concentration. Ostwald was inclined to attribute the lack of parallelism to secondary effects, especially to the accelerating influence of the sugar, which became greater the larger the proportion of sugar present relatively to acid. Water was left out of account.

In his memoir on the velocity of the inversion of cane sugar by acids, published in 1889, Arrhenius introduced the conception of an active mass and attributed the invertive power of acids to the free hydrogen ions; this conclusion has been somewhat fully considered in the paper by E. F. Armstrong and Caldwell, in which also reference was made to his later views published in 1899. It is noteworthy that in his "Allgemeine Chemie," published in 1889, Ostwald expressed the opinion that an acid inverts sugar because of the predisposing affinity of the acid for the alcoholic hydroxyls of the dextrose and levulose produced from the cane sugar. He appears, however, to have been at once converted by Arrhenius.

In 1897 it was contended by Cohen that the great increase in velocity in more concentrated solutions might be explained by assuming that, as in the case of gases, the space occupied by the molecules would be of consequence; he supposed the rate of inversion to be inversely proportional to the space at the disposal of the molecules.

In all cases, the method of treatment adopted by previous workers has been influenced, in the first place, by the prevailing practice of dealing with volume-normal solutions in laboratory work; and subsequently by the conception introduced by Van't Hoff that the state of the molecules of a substance in solution may be regarded as analogous to that of the molecules in a gas; *the fact being overlooked that as the concentration is varied the proportion of water present is also varied.* No attempt has been made to evaluate the chemical influence of the omitted water.

The extent to which the two methods of treatment afford different results will be at once apparent on reference to the upper half of the Diagram representing the results which I have obtained in a series of experiments—carried out in the manner described towards the close of this paper—which are summarised in Tables I, II and III.

When sugar and acid are dissolved together in water to a constant volume, solutions are obtained which undergo inversion at a rapidly increasing rate the more concentrated they are, the rate being an approximately linear function of the concentration (Equation 1, p. 288). When weight-normal solutions are used, no such rapid acceleration is observed, the rate being but slightly greater in concentrated solutions as compared with dilute solutions. In the former case, the weight of water present diminishes rapidly as that of the sugar is increased, practically following a linear law (Equation 2): the proportion of water, therefore, is varied both with reference to the sugar and to the acid. In the latter case, apart from changes in the bulk of the solution, only the sugar is varied, water and acid remaining constant.

No useful conclusion as to the nature of the processes operative in concentrated solutions can be drawn from the experiments carried out with volume-normal solutions until the results are reduced to weight-normal terms.

The results of a series of determinations of the electrical conductivity (molecular) of hydrogen chloride in presence of varying amounts of glucose are recorded in Tables IV, V and VI; the results when 1 gramme-molecular proportion of hydrogen chloride was present are also represented in the lower half of the Diagram. It will be seen that the difference is but small, due to the use, on the one hand of volume-normal solutions, on the other of weight-normal solutions; but this arises from the fact that the molecular conductivity of hydrogen chloride changes only to a slight extent on dilution. It should perhaps be pointed out that glucose was used in these experiments

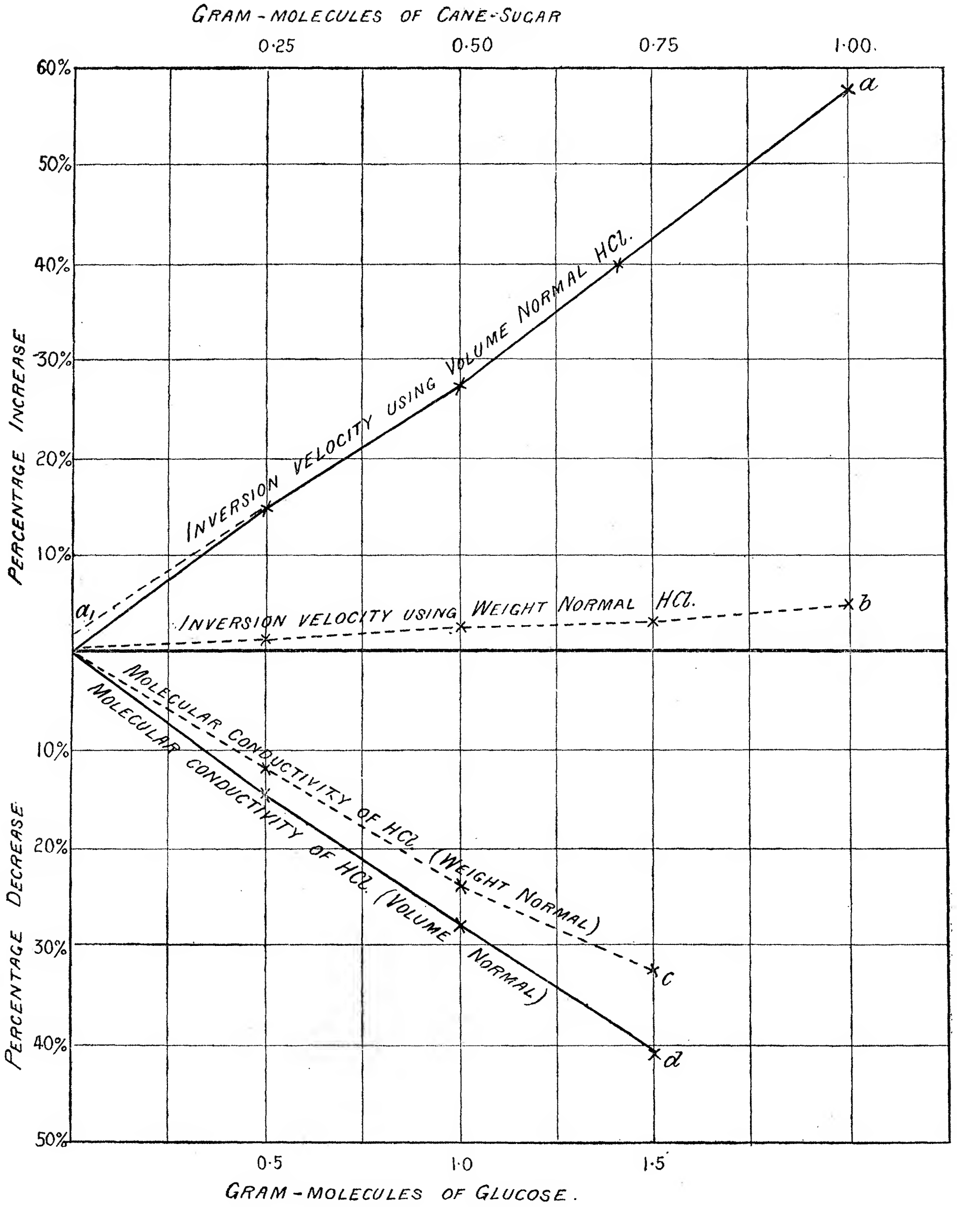

DIAGRAM.

The value obtained (490, Table III) by exterpolating the volume-normal curve on the assumption that the rate is a linear function of the concentration is, doubtless, somewhat low: hence the irregular character of the curve *a*. If the more probable value deduced from weight-normal solutions be taken as the origin (498), the curve becomes less irregular, as in curve a_1.

in place of cane sugar (*cf.* p. 280), as being its practical equivalent, in order to avoid the complications introduced by the changes attending inversion.

The fact that the effect of increasing the amount of the sugar is to increase the invertive power of the acid whilst it diminishes its conductivity is a strong argument against the application of the ionic hypothesis to hydrolysis, especially when taken in conjunction with the argument previously published in contrasting the hydrolytic activity of acids with that of enzymes.

The results of experiments which I have made to ascertain the influence of added substances on the rate of hydrolysis of cane sugar by an aqueous solution of chlorhydric acid are summarised in Table VII. The substances used were as follows:—

Lactose, Glucose, Glycerol, Alcohol, Potassium chloride, Ammonium chloride, Barium chloride, Calcium chloride, Sodium chloride, Acetic acid.

It will be seen that all these substances, excepting alcohol, have a more or less marked accelerating effect when used in volume-normal solutions, under conditions, that is to say, which involve more or less water being displaced by the added substance; when weight-normal solutions are used, glucose and lactose appear to have practically no effect, whilst glycerol and alcohol retard the change, all the remaining substances accelerating it.

In view of the general character of the effect produced by salts, bearing in mind also that easily soluble, hygroscopic salts, such as calcium chloride, have a far greater influence than sodium chloride, for example, it appears justifiable to regard the acceleration as a *concentration effect* due to the withdrawal by the dissolved substance of a certain proportion of the water molecules, which thus become removed from the sphere of action of the acid. To evaluate this effect I have determined the number of gramme-molecules of water which must be used in addition to the 1000 grammes originally taken, in order that the rate of change may be that characteristic of the solution prior to the addition of the "neutral" substance. These values are given in the last column of Table VII and are printed in thick type.

The explanations given by previous observers of the effects produced by added substances on the hydrolytic activity of acids have been of a varied character, but with scarcely an exception unsatisfactory and wholly biassed by ionic conceptions. Arrhenius[*] uniformly resorts to his idea of an "active part," which is either reduced or increased in amount to suit the conditions of the problem. Löwenthal and Lenssen,[†] who were the first to notice the accelerating effect of salts, attributed their action to the fixation of water and the consequent concentration of acid: hitherto, no one has accepted this explanation.

---

[*] 'Zeits. Phys. Chem.,' 1889, vol. 4, p. 226; 1899, vol. 28, p. 317.

[†] 'Journ. Prakt. Chem.,' 1862 (i), vol. 85, pp. 321 and 401.

To repeat the statement made in a previous paper*: "A very simple explanation of the action of acids may be given if the problem be considered from a point of view similar to that applied to enzyme action. In the first place, it may be assumed that *an active system* is formed by combination of part of the sugar with part of the acid—and as the water molecules in the solution are attracting both sugar and acid molecules, that there is, so to speak, competition between the water and the sugar for the acid; there will be, therefore, at any given temperature, an equilibrium between water, sugar and acid, depending on the relative proportions of these three constituents; a change in any one of them will necessarily also change the position of the equilibrium and therefore also the proportion of the combination of acid and sugar present."

Influence of Concentration on the Hydrolysis of Cane Sugar.—If the change be of this kind, in order to explain the gradual increase in the rate at which the cane sugar is hydrolysed as the solution is concentrated, it is necessary to consider the influence which an increase in the number of molecules of sugar present might exercise. From the point of view of the increased opportunity afforded to the acid, the rate of change should be proportional to the amount of sugar present; but if it be supposed that the sugar or indeed any substance present in the water is to some extent associated with the solvent, any increase in the amount of dissolved substance must involve a corresponding increase in the concentration of the substances participating in the interchange† and therefore must increase the rate of hydrolysis. Actually, this is what occurs. The observed increase in the rate cannot, however, be regarded as the absolute measure of the extent of the dehydrating influence of the sugar, as some portion of the latter may be present as an associated and, therefore, probably less active, if not inert, form.

In view of the presumed connection between osmotic pressure and rate of change, it may be pointed out here that, although the osmotic pressures determined by Morse and Frazer[*] in weight-normal solutions of cane sugar do not differ appreciably from the calculated values, the results which Lord Berkeley and Mr. Hartley[†] have brought before the Society recently, when calculated on a similar basis, appear to be somewhat above the calculated values, especially in the case of the more concentrated solutions.

---

* 'Roy. Soc. Proc.,' 1904, vol. 73, p. 533.

† As it is probable that the molecules are not all equally hydrated in solution, the sugar molecules themselves may be less hydrated in a more concentrated solution: it may be that the less hydrated or anhydrous molecules are the more open to attack by the acid. Perhaps this assumption might account for the effect of high pressures on the inversion velocity, which effect has hitherto failed to receive a satisfactory explanation. Röntgen ('Wied. Ann.,' 1892, vol. 45, p. 98), Stern ('Ann. Phys. Chem.,' 1898, vol. 59, p. 652) and Rothmund ('Zeits. Phys. Chem.,' 1896, vol. 20, p. 168) have independently recorded the fact that a high pressure decreases the inversion velocity to the extent of 1 per cent. per 100 atmospheres, although both the "ionisation" and the "ionic mobility" are increased. It may well be that the degree of hydration of the sugar is increased by pressure and that under a high pressure the sugar, being more highly hydrated, would be less open to attack and the inversion slower in consequence.

My observations appear to afford considerable support to the results arrived at by the English observers. On the other hand, taken in conjunction with my results, the conclusion at which they have arrived may be held to elevate the assumption that the sugar molecules are hydrated almost to the level of certainty.

Influence of Alcohol.—A single molecular proportion of alcohol per litre, in a volume-normal solution, is *apparently* without influence; inasmuch, however, as it displaces almost its own volume of water in the solution, it must be held to have a considerable retarding effect. That this is the case is seen on reference to the result obtained in weight-normal solution, the value being reduced from $K = 510$ to $K = 467$.

Using larger proportions of alcohol, previous observers[‡] have noticed a retarding effect even in volume-normal solutions; the explanations which have been offered of its influence are in no way satisfactory. In certain cases alcohol has been shown to have a marked accelerating effect, as in the formation of urea from ammonium cyanate.[§]

Alcohol may be pictured as acting in at least three ways:—(1) Mechanically, by its interposition between the acting substances; (2) as exercising a concentrating effect such as the sugars exercise by combining with water; (3) as entering into association with the active agent, viz., hydrogen chloride, forming an "alcoholate." Of these (1) and (3) would be unfavourable, whilst (2) would accelerate the change. There is every reason to suppose that all three influences are operative and that the concentrating effect of alcohol is more than counterbalanced by the extent to which it interferes mechanically and (probably) more especially by the formation of an alcoholate.

Influence of Glycerol.—Although apparently, in volume-normal solution, glycerol has a slight accelerating influence, the effect is more than accounted for by the amount of water which it displaces. Considered from the rational standpoint, *i.e.*, in weight-normal solutions, it has a distinct retarding effect, which is considerably less, however, than that of alcohol. The arguments used in respect of alcohol are also applicable to glycerol; it may again be supposed that the retardation is mainly due to a withdrawal of some part of the hydrogen chloride in loose combination with the alcohol. The readiness with which glycerol is attacked by acids is in harmony with this explanation.

---

[*] 'Amer. Chem. Journ.,' 1905, vol. 34, p. 1.

[†] 'Roy. Soc. Proc.,' 1906, A. vol. 77, p. 156.

[‡] Compare Kablukow and Zacconi, 'Journ. Russ. Chem. Soc.,' 1891, vol. 23, p. 546; Wakeman, 'Zeits. Phys. Chem.,' 1893, vol. 11, p. 49; Cohen, *ibid.*, 1898, vol. 25, p. 1; Arrhenius, *ibid.*, 1899, vol. 28, p. 317.

[§] Walker and Kay, 'Chem. Soc. Trans.,' 1897, vol. 71, p. 489.

Influence of Glucose.—A series of experiments, the results of which are not quoted, showed that in volume-normal solution the effect of a single gramme-molecular proportion of the allied substances glucose, galactose and mannitol is practically identical. Moreover, glucose can be substituted for cane sugar almost weight for weight in volume-normal solutions without sensible change in the rate at which the cane sugar is hydrolysed, whatever the proportions present. But inasmuch as glucose displaces slightly more water than cane sugar the results obtained with weight-normal solutions are slightly lower in presence of glucose. Thus, the constant K is lowered from 521, the value given by a gramme-molecular proportion of cane sugar, to 518 by substituting for half the cane sugar a gramme-molecule of glucose.

Seeing that the glucose must interfere mechanically, the glucose must be supposed to be at least as highly hydrated as the approximately equal weight of cane sugar. There is no reason to suppose that it will differ much from the cane sugar in its affinity for the acid.

It is very noteworthy that in all cases the constant K has practically the same value throughout the course of an experiment (*vide* Tables X and XI). Hence it follows that whatever changes take place in the solution the influence exercised by the products of change must be almost exactly equal to that exercised by the sugar originally present which undergoes hydrolysis in accordance with the equation :—

$$C_{12}H_{22}O_{11} + OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6},$$

It is obvious that the argument already used with reference to glucose will apply equally well to fructose; and inasmuch as the two molecules of hexose are even superior in dehydrating power to a single molecule of cane sugar, it would seem to follow that most, if not all, of the oxygen atoms exercise an influence on water molecules.

Bearing in mind the complex nature of the influences at work, it is altogether remarkable that the simple monomolecular law should be found to hold throughout;* this result may serve to show how very necessary it is to exercise caution in judging from apparently simple results as to the true nature of the underlying phenomena. It may be expected that more concentrated solutions will give results showing an *increase* in velocity as the hydrolysis proceeds, owing to the fact that the proportion of water which enters into combination will be a sufficiently important fraction of the total water present to influence the rate. Experiments to test this conclusion are in progress.

---

* *Vide* Mellor and Bradshaw, 'Zeits. Phys. Chem.,' 1904, vol. 48, p. 353.

Influence of Lactose (Milk Sugar).—In volume-normal solution the addition of half a molecular proportion of lactose* to the same amount of cane sugar, although it gives rise to the displacement of slightly more water, has actually less effect than the cane sugar; in other words, lactose is less effective as a dehydrating agent than cane sugar. This conclusion is in harmony with the recognised character of the substance, especially its moderate solubility, which may be regarded as an indication of a tendency to form relatively inert, associated molecules.

In weight-normal solutions it is apparently without effect; in other words, it exercises a dehydrating influence which is only sufficient to balance the small reduction in activity brought about by its mechanical interference.

Influence of Acetic Acid.—As this acid has practically no hydrolytic effect on cane sugar in comparison with the effect of chlorhydric acid, it is possible to determine its influence as a "neutral" substance. It will be seen that it exercises a slight concentrating effect equivalent to the withdrawal of a single molecule of water by each molecule of acetic acid. This is entirely in accordance with its known behaviour as a weak dehydrant.

Influence of Salts.—Salts have uniformly a concentrating effect; the addition of a molecular proportion of calcium chloride to a volume-normal solution more than doubles the rate of change.

To determine the "degree of hydration" of the salt, the extent to which it was necessary to dilute the weight-normal solutions in order to reduce the value of the constant K to 510—the standard value—was determined in each case. The values arrived at are as follows:—

$NH_4Cl\ 10H_2O$ $KCl\ 10H_2O$ $NaCl\ 13H_2O$
$BaCl_2\ 19H_2O$ $CaCl_2\ 22H_2O$

These values are necessarily somewhat low, as no allowance can be made for the mechanical interference of the salt. They are clearly rational values, however; moreover, they are in accordance with estimates arrived at in other ways.

The results obtained by H. C. Jones and his colleagues,† although confirmatory of the values now arrived at in the case of calcium chloride and probably also of barium chloride, are not in harmony with them in respect of other substances. The literature on the subject is so voluminous that it cannot be discussed in an adequate manner on the present occasion; but it may be pointed out that the method described in this communication is one which involves only the consideration of the effect produced on the cane sugar, whereby a measure is secured (in the case of salts) of the concentration effect from which the average degree of hydration of the salt is inferred without reference to the condition of this salt in solution. The method of calculation adopted by H. C. Jones, however, is one which does not in itself permit of any line being drawn between effects produced on the one hand by hydration and on the other by polymerisation.

---

* No exception to the use of lactose in this connection can be taken on the ground that it would be attacked by the acid and thus give rise to complications. Under the conditions of the experiments, no appreciable hydrolysis of lactose occurs during 24 hours. (*Vide* 'Roy. Soc. Proc.,' 1904, vol. 73, p. 530.)

† 'Amer. Chem. Journ.,' 1904, vol. 32, p. 310; 1905, vol. 33, p. 548; 1906, vol. 35, p. 445.

From this point of view, it may be noticed on comparing the degree of hydration of potassium and sodium chlorides and of barium and calcium chlorides that the more soluble salt of each pair is more hydrated. It is probable that in most cases the less soluble salt is present in solution to the greater extent in a polymerised form.

It is scarcely necessary to add that the values given in Table VII apply only to the particular degree of concentration which was studied. It may be expected that in more dilute solutions the "degree of hydration" would be greater, whilst in more concentrated solutions it would be less.

The limits of variation in the case of sodium chloride are relatively small, as shown in Table VIII, in which is given the average degree of molecular hydration in solutions containing from 1 to 5 gramme-molecular proportions of salt.

Conductivity as Influenced by the Presence of Non-electrolytes.

The equations given in Table IX represent the results obtained in a series of experiments which were made with the object of ascertaining the influence of various carbohydrates on the electrolytic conductivity of solutions of hydrogen chloride and of sulphuric acid, with a view of ascertaining in what way the condition of the acid might be influenced. The effect is in all cases of the same order, equal weights having practically the same effect in lowering the conductivity.

Down to N/8 strength the proportional influence of the dissolved substance is independent of the concentration of the acid; at high dilutions ($v = 128$) as shown in Tables XII to XV, the added substance produces a greater proportionate effect than in the more concentrated solutions.

In all probability the effect of the added substance is mainly mechanical in the more dilute solutions, however, the non-electrolyte apparently has a distinct dehydrating effect on the acid.

Experiments are being carried out to determine the influence of chlorides on the conductivity of hydrogen chloride, in order to ascertain whether their influence may not also be regarded in the light of the view put forward in this communication. This is the more desirable, inasmuch as it is clear that the influence of salts on the hydrolysis of cane sugar by acids is incompatible with the view which is commonly held that a neutral salt diminishes the extent to which the acid undergoes electrolytic dissociation in solution.

EXPERIMENTAL.

Materials Used.—An approximately twice normal solution of pure hydrogen chloride was used, which was standardised by titration with baryta against a solution prepared by Moody's absolute method;* the conductivity of the acid was determined from time to time in order to ascertain whether any alteration had taken place. A few measurements were made with sulphuric acid which had been standardised by Marshall's method.†

The purest obtainable centrifugalised crystals of cane sugar were used; this material did not reduce Fehling's solution.

The milk sugar was crystallised from 50 per cent. alcohol; the conductivity of a solution containing $\frac{1}{2}$ gramme-molecule of the sugar dissolved in one litre of water was 0·000030 reciprocal ohms.

Kahlbaum's purified glucose, mannitol and galactose were used; these were all tested by the conductivity method. In determining the conductivity of these carbohydrates, a difficulty arises from the fact that, in presence of the platinum black of the electrodes, they are slowly oxidised, giving products which are better electrolytes. It was, therefore, necessary to determine the conductivity at different intervals of time and to exterpolate, to determine the conductivity at the moment of putting the solution into the measuring cell. The conductivity of solutions of one gramme molecular proportion of each sugar in a litre of solution determined in this manner was, in the case of glucose, 0·000043 reciprocal ohms, in that of mannitol 0·000046 and in that of galactose 0·000064 reciprocal ohms. On account of the relatively high conductivity, it was suspected that galactose contained some alkaline impurity, especially as it was found to produce an abnormally large diminution in the conductivity of N/128 hydrochloric acid. To purify it, 80 grammes were dissolved in 60 c.c. of water by heating the mixture;

---

* 'Chem. Soc. Trans.,' 1898, vol. 73, p. 658.

† 'Soc. Chem. Ind.,' 1899, vol. 18, p. 4.

200 c.c. of methyl alcohol were then added to the cooled solution, and carbon dioxide was bubbled into the liquid, which was subsequently filtered and allowed to crystallise; the latter process occupied a considerable time. The galactose was washed with methyl alcohol and dried during two weeks *in vacuo* over potash. In this manner the conductivity of the gramme-molecular solution was reduced to 0·000035 reciprocal ohms.

The salts used were recrystallised until neutral, excepting the calcium chloride, which contained a little free alkali; this salt was always carefully neutralised with the predetermined amount of centinormal chlorhydric acid before starting the inversion.

Temperature.—The temperature gradient for the inversion of cane sugar is so large that it is important that the temperature should be very carefully regulated. The inversion experiments were carried out in a polarimeter tube which was maintained at 25° by a stream of water from a thermostat. The arrangements are depicted in fig. 1. Water taken from a low-pressure main at a temperature varying between 10° and 18° was first passed through a condenser A in which it was warmed by the waste water returning from the polarimeter tube. Thence it passed to the bottom of the funnel-shaped vessel B, made of sheet copper, which contained a rough toluene thermo-

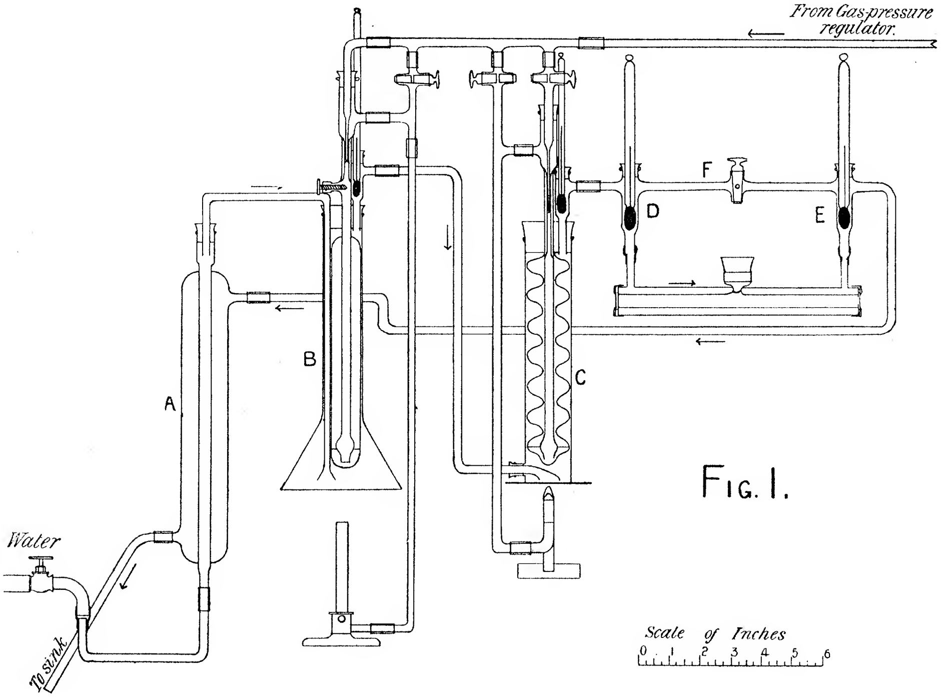

Fig. 1.

regulator in connection with a bunsen flame beneath the vessel; the stream of water was heated to an approximately constant temperature of 24° in this vessel. It then passed into the bottom of the cylindrical vessel C, also made of sheet copper and flanged at the bottom; this vessel is almost filled by a sensitive toluene thermo-regulator with fluted sides; a small flame beneath the vessel in connection with the regulator served to heat the stream of water to a constant temperature of 25°. The water thus heated passed through the small chamber D containing a sensitive thermometer and thence directly into the jacket of the polarimeter tube. The temperature of the waste water was also read in E. When the polarimeter tube was removed, the stream of water could be diverted through the tube F. In order to reduce the loss of heat to a minimum, the vessels A, B, C, D and E and also the polarimeter tube were packed round with felt. The whole apparatus was placed in a room kept at a constant temperature of 20° (at the level of the polarimeter) by means of a gas stove controlled by a large thermo-regulator shaped like a gridiron and filled with saturated solution of calcium chloride.

The temperature of the liquid in the polarimeter tube was found to oscillate 0°·02 C. on each side of the mean temperature, 25°·00 C., in regular periods of about 1·4 minutes. In experiments which extend over an hour, this small variation is of no importance. The drop in temperature of the stream whilst passing through the jacket was negligible.

The conductivities were determined in a large thermostat maintained at 25° C. by means of the spiral toluene thermo-regulator described by Lowry.* It was found to be of advantage to use a gas-pressure regulator with the former thermostat; a very simple and satisfactory device for this purpose is shown in fig. 2. The gas is introduced from the main by tube *a* and passes over the surface of the mercury in the cup *b*, which is firmly fixed to the inner bell-jar by a glass rod *c*; this rod is continued upwards and slides in the fixed tube *d*, which serves as a guide for the floating bell-jar. The pressure of the gas escaping through *e* is that given by the difference in level between the water inside and outside the floating jar and is arranged to be less than the minimum pressure of the gas in the mains. When this regulator is at work the inner bell-jar is in a state of continuous vibration: the gas is therefore passed into a Winchester quart bottle which serves as a buffer; it escapes as a stream of gas at the steady constant pressure indicated by the gauge glass *f*.

Method of Making the Inversion Experiments.—The exact quantity of sugar required together with any additional substance was weighed out for each experiment. The solids were then carefully transferred to a weighed 50-c.c.

---

* 'Chem. Soc. Trans.,' 1905, vol. 87, p. 1030.

standard flask with water of low conductivity and dissolved in about 24 c.c. by heating the liquid to the boiling point. After cooling, the exact amount of twice normal chlorhydric acid (25 c.c.) was run in from a standard burette and the whole made up to 50 c.c. at 25°. The flask and its contents were then weighed again, in order that the weight of water in a litre of solution could be calculated. When a weight-normal solution was required, a 50-c.c. flask was used which had a bulb blown on the neck above the graduation mark. The exact amount of water could then be run in from a burette to make the total up to 50 grammes of water after the 50 c.c. of solution had been weighed. The well-mixed solutions were then filtered directly into the polarimeter tube at 25° C. and allowed at least 10 minutes to attain to the temperature of the thermostat before taking the first reading. Rotations were then taken—15 in all, in each experiment—at 30, 35, 40—100 minutes after the first and the final reading after 24 hours, by which time the rotation had reached its minimum. Each of the recorded rotations is the mean of five readings taken at minute and half-minute intervals on each side of the mean time. The 65 hydrolyses herein recorded thus represent over 5500 polarimeter readings. The error in the value of the constant for each experiment is certainly very small, as will be obvious on reference to Tables X and XI, which are entirely representative of the results obtained in each separate experiment; on this account, it is thought to be unnecessary to reproduce more than four complete sets of the observed values as specimens of the actual course of the experiments. In cases in which the results are not in close accordance, the discrepancy should be attributed rather to differences in the preparation of the solutions than to errors in the determination of the velocity.

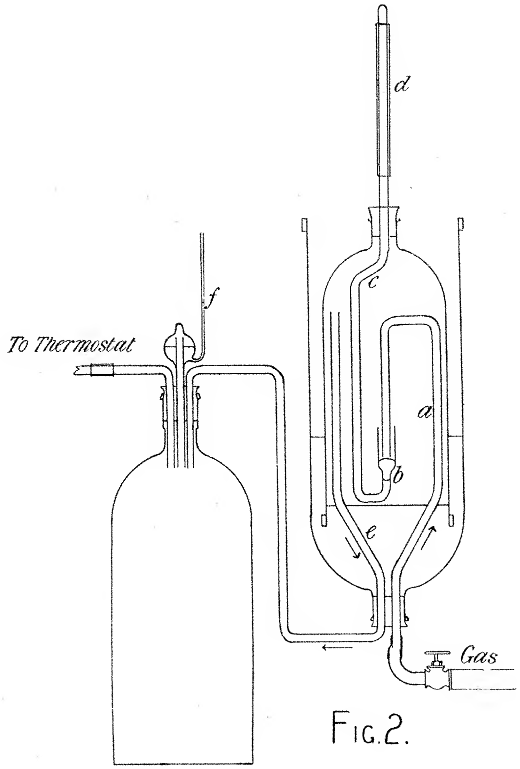

FIG. 2.

Conductivity Measurements.—The measurements of conductivity recorded in Tables IV, V, XII, XIII, XIV and XV were made in a U-tube resistance cell of the ordinary type, using the Kohlrausch wheel bridge, inductorium and telephone. It was found to be of advantage to insert a liquid rheostat in the telephone circuit, which had no influence on the reading but enabled the noise in the receiver to be altered at will, thus securing greater accuracy.

In all cases the calculation was of the following type:—

N/8 chlorhydric acid.	18 grammes glucose in 1000 grammes water =1116·8 c.c.
Resistance of coils........................	100·0 ohms.
Reading of bridge-wire..................	536·6 „
Resistance	115·84 „
Less resistance of leads	0·09 „
Resistance of cell	115·75 „
Specific conductivity	0·03250
Less { conductivity of glucose.........	0·000043
„ water	0·000003
Conductivity of N/8 HCl	0·032454

The values given in the tables are multiplied by 1000.

The measurements with N/128 acids were made in a cell of the 'Arrhenius' type.

Table I.—Inversion Velocities, using 1 gramme-molecule of Hydrogen Chloride.

Gramme-molecules of cane sugar.	Volume of solution = 1 litre.			Solution in 1000 grammes of water.		
	Velocity constant.	Mean K.	Weight of water.	Velocity constant.	Mean K.	Volume of solution.
			grammes.			c.c.
0·25 (85·5 grammes)	557 563	560	929·4	504 504	504	1069·4
0·5 (171 grammes)	624 621	622	876·7	508 512	510	1122·6
0·75 (256·5 grammes)	696 699	698	824·4	514 512	513	1175·4
1·0 (342 grammes)	768 772	770	771·8	520 522	521	1228·2

Table II.—Inversion Velocities and Weights of Water per Litre of Solution, using 1 gramme-molecule of hydrogen chloride and varying the amount of cane sugar in 1 litre.

Gramme-molecules of cane sugar.	Mean velocity constant.	Calculated velocity constant. (Equation 1.)	Mean weight of water.	Calculated weight of water. (Equation 2.)
			grammes.	grammes.
0·25	560	560	929·4	930·6
0·5	622	630	876·7	877·4
0·75	698	700	824·4	824·6
1·0	770	770	771·8	771·8

Equation 1—

$$K_m = 490\ (1+0{\cdot}5714\ m)\ \text{grammes};$$

Equation 2—

$$\text{Water per litre} = (1000-17{\cdot}1-211{\cdot}1\ m)\ \text{grammes};$$

where K_m is the inversion velocity for a solution of m gramme-molecule of cane sugar per litre.

Table III.—Relative Rates of Inversion by Hydrogen Chloride of various Concentrations of Cane Sugar in Volume-normal and Weight-normal Solutions.

Gramme-molecules of cane sugar.	Volume-normal.		Weight-normal.	
	Velocity constant.	Relative velocity constant.	Velocity constant.	Relative velocity constant.
1·00	770	1·571	521	1·046
0·75	697	1·422	513	1·030
0·50	622	1·269	510	1·024
0·25	560	1·143	504	1·012
—	Calc. (490)	1·000	Calc. (498)	1·000

Table IV.

Conductivity of Chlorhydric Acid in presence of Glucose (volume-normal).

Glucose in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.				
	1.	2.	4.	8.	128.
270	193·3	105·2	55·09	28·32	—
180	235·8	127·7	67·09	34·50	2·266
90	280·0	152·2	79·93	41·17	2·736
0	327·9	178·3	93·61	48·22	3·211

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No glucose.	1·5 gramme-molecule glucose per litre.			1 gramme-molecule glucose per litre.			0·5 gramme-molecule glucose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327 ·9	193 ·3	193 ·3	—	235 ·8	235 ·1	0 ·7	280 ·0	280 ·0	—
2	356 ·6	210 ·4	210 ·2	0 ·2	255 ·4	255 ·7	−0 ·3	304 ·4	304 ·5	−0 ·1
4	374 ·4	220 ·4	220 ·7	−0 ·3	268 ·4	268 ·4	—	319 ·7	319 ·7	—
8	385 ·8	226 ·6	227 ·4	−0 ·8	276 ·0	276 ·6	−0 ·6	329 ·4	329 ·4	—
128	411 ·0	—	—	—	290 ·0	294 ·7	−4 ·7	350 ·2	350 ·9	−0 ·7

$$C_m = C_0 (1 - 0{\cdot}3017m + 0{\cdot}01865m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the glucose per litre.

Table V.—Conductivity of Chlorhydric Acid in presence of Glucose (weight-normal).

Glucose in grammes per kilogramme of water.	Dilution of acid in kilogrammes of water per gramme-molecule of HCl.			
	1.	2.	4.	8.
27	184 ·8	99 ·25	52 ·18	26 ·79
18	221 ·4	120 ·7	62 ·94	32 ·45
9	265 ·9	147 ·0	76 ·18	39 ·48
—	320 ·8	178 ·9	93 ·21	48 ·23

Molecular Conductivities (weight-normal).

Glucose in grammes per kilogramme of water.	Dilution in kilogrammes of water per gramme-molecule of HCl.			
	1.	2.	4.	8.
27	220 ·2	234 ·8	245 ·8	251 ·9
18	251 ·2	271 ·3	281 ·5	290 ·1
9	286 ·7	313 ·9	324 ·3	334 ·9
—	327 ·4	362 ·2	375 ·7	389 ·9

$$C_m = C_0 (1 - 0{\cdot}290m + 0{\cdot}0445m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of glucose per kilogramme of water.

Table VI.—The Relative Electrical Conductivities in presence of varying Amounts of Glucose of Chlorhydric Acid in Volume-normal and Weight-normal Solutions of Hydrogen Chloride.

Gramme-molecules of glucose.	Volume-normal.		Weight-normal.	
	Molecular conductivity.	Relative conductivity.	Molecular conductivity.	Relative conductivity.
1 ·5	193 ·3	0 ·590	220 ·2	0 ·673
1 ·0	235 ·8	0 ·719	251 ·2	0 ·767
0 ·5	280 ·0	0 ·854	286 ·7	0 ·876
—	327 ·9	1 ·000	327 ·4	1 ·000

Table VII.—Inversion Velocities, using 0·5 gramme-molecule of Cane Sugar, 1 gramme-molecule of Hydrogen Chloride and 1 gramme-molecule of added Material (unless otherwise stated).

Added substance.	Volume of solution = 1 litre.		Solution in 1000 grammes of water.		Solution in 1000 grammes + X gramme-molecules of water.	
	K.	Weight of water.	K.	Volume of solution.	K.	X.
		grammes.		c.c.		
—	624	877 ·4	508	1122 ·6		
—	621		512			
Glucose (½ gramme-molecule)	694	820 ·3	515	1179 ·7		
	698		514			
Glucose (1 gramme-molecule)	—	—	517	1242 ·8		
			519			
Glycerol..............	654	801 ·0	485	1198 ·4		
Alcohol	623	818 ·8	467	1182 ·4		
Lactose (½ gramme-molecule)	725	767 ·6	510	1233 ·2	494	$1H_2O$
KCl	906	845 ·8	671	1154 ·2	539	$8H_2O$
	897		682		538	
					521	$9H_2O$
					508	**$10H_2O$**
NH_4Cl	907	833 ·4	666	1167 ·0	521	$9H_2O$
					510	**$10H_2O$**
NaCl	963	858 ·6	738	1141 ·4	**507**	**$13H_2O$**
	963		725		**509**	
$BaCl_2$.................	—	—	—	1164 ·2	468	$22H_2O$
					496	$20H_2O$
					495	
					507	**$19H_2O$**
$CaCl_2$.................	1313	844 ·1	980	1156 ·1	626	$15H_2O$
			983		**511**	**$22H_2O$**
					511	
$CH_3.COOH$	692	821 ·2	521	1179 ·6	**507**	**$1H_2O$**

Table VIII.—Inversion Velocities, using 0·5 gramme-molecule of Cane Sugar, 1 gramme-molecule of Hydrogen Chloride and 1000 grammes of Water, together with a variable number of gramme-molecules of additional Water and of Sodium Chloride.

Gramme-molecules of NaCl.	Gramme-molecules of additional water.	Total volume of solution.	K.	Average hydrate of NaCl.
		c.c.		
1	—	1141·4	738	
			725	
	13	1375·4	507	
			509	$NaCl\ 13H_2O$
3	33	1786·4	513	$NaCl\ 11H_2O$
	36	1840·2	486	
5	25	1687·8	917	
	45	2040·2	561	
	48	2093·8	515	$NaCl\ 9{\cdot}6H_2O$

Table IX.—Equations representing the Influence of Carbohydrates on the Conductivity of Chlorhydric and Sulphuric Acids of Concentration varying between 1 gramme-molecule and $\frac{1}{8}$ gramme-molecule per litre (volume-normal).

Chlorhydric Acid.

Glucose .... $C_m = C_0(1-0{\cdot}3017m+0{\cdot}01865m^2)$.

Galactose .... $C_m = C_0(1-0{\cdot}2902m+0{\cdot}0148m^2)$.

Mannitol .... $C_m = C_0(1-0{\cdot}2902m+0{\cdot}0101m^2)$.

Milk sugar............ $C_m = C_0(1-0{\cdot}5563m+0{\cdot}0768m^2)$.

Sulphuric Acid.

Glucose .... $C_m = C_0(1-0{\cdot}2927m+0{\cdot}0077m^2)$.

C_m represents the conductivity of a solution of acid containing m gramme-molecules of added sugar in a litre of solution.

Table X.—Inversion Experiments at 25° C. with 1 gramme-molecule of HCl.

Time in minutes.	Solution contains— 1 gramme-molecule of cane sugar + 772·1 grammes of water in 1 litre.		Solution contains— 1 gramme-molecule of cane sugar + 1000 grammes of water in 1228·2 c.c.	
	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.
0	32° 7′	—	30° 47′	—
30	12 44	766	17 57	519
35	10 27	763	16 16	518
40	8 11	768	14 38	518
45	6 6	774	13 5	519
50	4 13	777	11 36	520
55	2 38	774	10 16	519
60	1 7	775	8 57	521
65	−0 14	773	7 46	520
70	−1 31	774	6 37	520
75	−2 38	772	5 36	519
80	−3 40	771	4 30	522
85	−4 40	773	3 34	521
90	−5 33	773	2 42	520
95	−6 22	773	1 49	522
100	−7 3	770	1 3	521
∞	−15 4	—	−11 47	—
	Mean	772	Mean	520

Table XI.—Inversion Experiments at 25° C. with 1 gramme-molecule of HCl.

Time in minutes.	Solution contains— 1 gramme-molecule of cane sugar, 1 gramme-molecule of alcohol + 818·8 grammes of water in 1 litre.		Solution contains— 1 gramme-molecule of cane sugar, 1 gramme-molecule of calcium chloride + 844·1 grammes of water in 1 litre.	
	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.
0	17° 15′	—	9° 58′	—
30	8 43	621	−1 27	1313
35	7 34	625	−2 35	1320
40	6 33	624	−3 32	1325
45	5 36	624	−4 19	1322
50	4 43	624	−4 58	1314
55	3 55	622	−5 31	1306
60	3 7	624	−6 4	1314
65	2 26	622	−6 30	1313
70	1 45	623	−6 52	1310
75	1 8	622	−7 11	1308
80	+0 33	623	−7 27	1304
85	+0 1	623	−7 43	1313
90	−0 27	620	−7 56	1317
95	−0 55	620	−8 5	1306
100	−1 22	621	−8 14	1304
	−7 13	—	−9 11	—
	Mean	623	Mean	1313

Table XII.

Conductivity of Chlorhydric Acid in presence of Galactose (volume-normal).

Galactose in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.					
	1. A.	2. A.	4. A.	8. A.	128. A.	128. B.
180	238 ·1	130 ·1	67 ·69	34 ·97	2 ·138	2 ·255
90	281 ·3	153 ·9	80 ·57	41 ·27	2 ·647	2 ·726
0	327 ·9	179 ·4	93 ·67	48 ·39	3 ·211	3 ·211

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No galactose.	1 gramme-molecule galactose per litre.			0·5 gramme-molecule galactose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327 ·9	238 ·1	237 ·6	0 ·5	281 ·3	281 ·5	− 0 ·2
2	358 ·8	260 ·2	260 ·0	0 ·2	307 ·8	308 ·1	− 0 ·3
4	374 ·7	270 ·8	271 ·5	− 0 ·7	322 ·3	321 ·7	0 ·6
8	387 ·1	379 ·8	280 ·5	− 0 ·7	330 ·2	332 ·4	− 2 ·2
*128 A	411 ·0	273 ·7	297 ·8	−24 ·1	338 ·8	352 ·9	−14 ·1
128 B	Puriss. galactose	288 ·6	297 ·8	− 9 ·2	348 ·9	352 ·9	− 4 ·0

$$C_m = C_0(1 - 0{\cdot}2902m + 0{\cdot}0148m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the galactose per litre.

Table XIII.

Conductivity of Chlorhydric Acid in presence of Mannitol (volume-normal).

Mannitol in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.				
	1.	2.	4.	8.	128.
182	235 ·9	129 ·3	67 ·43	34 ·71	2 ·234
91	281 ·0	153 ·9	80 ·32	41 ·30	2 ·693
0	327 ·9	179 ·4	93 ·67	48 ·39	3 ·211

---

* Impure material, *vide* p. 283.

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No mannitol.	1 gramme-molecule mannitol per litre.			0·5 gramme-molecule mannitol per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327·9	235·9	236·1	−0·2	281·0	281·1	−0·1
2	358·8	258·6	258·3	0·3	307·8	307·6	0·2
4	374·7	269·7	269·7	—	321·3	321·3	—
8	387·1	277·7	278·7	−1·0	330·4	331·9	−1·5
128	411·0	286·0	295·9	−9·9	344·7	352·4	−7·7

$$C_m = C_0(1 - 0{\cdot}2902m + 0{\cdot}0101m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the mannitol per litre.

Table XIV.

Conductivity of Chlorhydric Acid in presence of Lactose (volume-normal).

Lactose in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.				
	1.	2.	4.	8.	128.
180	243·0	133·3	69·40	35·59	2·309
90	283·3	155·4	81·31	41·89	2·750
0	327·9	179·4	93·67	48·39	3·211

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No lactose.	0·5 gramme-molecule lactose per litre.			0·25 gramme-molecule lactose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327·9	243·0	243·0	—	283·3	283·9	−0·6
2	358·8	266·6	265·9	0·7	310·8	310·6	0·2
4	374·7	277·6	277·7	− 0·1	325·2	324·4	0·8
8	387·1	284·7	286·9	− 2·2	335·1	335·1	—
128	411·0	278·9	304·6	−25·7	352·0	355·8	−3·8

$$C_m = C_0(1 - 0{\cdot}5563m + 0{\cdot}0768m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of lactose per litre.

Table XV.

Conductivity of Sulphuric Acid in presence of Glucose (volume-normal).

Glucose in grammes per litre.	Dilution of acid in litres per gramme-molecule.				
	1.	2.	4.	8.	128.
180	276 ·5	150 ·8	78 ·03	40 ·72	3 ·467
90	330 ·5	180 ·7	93 ·33	48 ·90	4 ·234
0	385 ·5	211 ·2	109 ·3	57 ·56	5 ·021

Molecular Conductivities of Sulphuric Acid.

Dilution of H_2SO_4.	No glucose.	1 gramme-molecule glucose per litre.			0·5 gramme-molecule glucose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	385 ·5	276 ·5	275 ·7	0 ·8	330 ·5	329 ·8	0 ·7
2	422 ·4	301 ·6	302 ·1	− 0 ·5	361 ·4	361 ·4	—
4	437 ·2	312 ·1	312 ·6	− 0 ·5	373 ·3	374 ·1	−0 ·8
8	460 ·5	325 ·8	329 ·3	− 3 ·5	391 ·2	394 ·0	−2 ·8
128	642 ·7	443 ·8	460 ·9	−17 ·1	542 ·0	549 ·9	−7 ·9

$$C_m = C_0 (1 - 0{\cdot}2927m + 0{\cdot}00776m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the glucose per litre.